Chip based Fabrication of Flexible Microfiber and Mechanical Characterization

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Abstract—**Recently, chip based fabrication of curved microstructures, such as microsphere, microfiber and microtube, has attracted much attention owing to their many advantages. In this paper, we have fabricated pH-responsive flexible microfiber using the microfluidic chip and 'on the fly' photopolymerization method, and we characterized their mechanical and swelling properties. First, we have measured the swelling properties according to the pH variation. The PDMS based test apparatus was prepared, and we inserted the microfiber and measured the volume transitions. The shrinking and the swelling motions were measured according to the different sized (50, 80, 100μm) fibers to investigate the size effect. The effects of acrylic acid (AA, pH sensitive monomer) concentration were examined also. As the fibers' diameter increases, the response of volume transition was slow, and higher AA showed larger volume expansion to the application of basic solution. Second, we have measured the elasticity of microfiber according to AA concentration (weight %: 6, 11, and 22). The elasticity at the fiber having less AA concentration was larger, and this indicates that the fiber having lower AA concentration is softer. The advantages of our fabrication method are as follows; 1) the process is simple and cost effective, 2) we can functionalize the fiber and this can be applied to diverse microdevices such as sensors or actuators, 3) the size can be easily altered via the regulation of flow rate. Here, we showed the fibers' mechanical properties, and we expect that the microfiber can be applied to the fabrication of artificial muscle.**

Keywords—**pH-responsive, microfiber, photopolymerization, artificial muscle.**

I. Introduction

In nature, the most important components of a living cell (proteins, carbohydrates, and nucleic acids) are polymers [1], which function broadly as parts of complicated cell machinery. Among man-made products, ionic hydrogels exhibit a volumetric change in response to certain stimuli such as pH, temperature, and the concentration of an organic solvent, and these hydrogels' actuating mechanism is very similar to the mechanism underlying living organisms [2-3]. Researchers have made broad use of such stimulus-responsive hydrogels in many fields and have reported on diverse applications, including valves [4], drug-delivery actuators [5], self-regulating devices [6], and artificial muscles [7]. Recently, researchers in diverse fields have applied *in-situ* photopolymerization to the construction of such hydrogel structures inside microfluidic platforms. This approach has attracted a great deal of attention owing to both the simplicity of the fabrication process and the cost effectiveness of the fabrication process relative to conventional fabrication technology [8-9]. In this paper, we have presented a method for the mass production of pH-responsive microfibers that act as actuating elements and we have characterized their swelling properties. For the mass production of the microfibers, we used the 'on the fly' photopolymerization method. First, we characterized the microfibers' swelling properties under diverse conditions: 1) microfibers' repeated swelling and shrinking motions as responses to pH-value changes, 2) microfibers' swelling properties as responses to the change of microfiber' size (50, 80, 100μm), and 3) microfibers' swelling properties as responses to the change of acrylic acid (AA, pH sensitive monomer) concentration. Second, we have measured the elasticity of microfiber according to AA concentration (weight %: 6, 11, and 22). The elasticity at the fiber having less AA concentration was larger, and this indicates that the fiber having lower AA concentration is softer. The suggested fabrication method for microfibers has many advantages such as (1) the process is simple and cost effective, (2) we can functionalize the fiber and this can be applied to diverse microdevices such as sensors or actuators, (3) the size can be easily altered via the regulation of flow rate. Here, we showed the fibers' mechanical properties, and we expect that the microfiber can be applied to the fabrication of artificial muscle.

II. Fabrication and Method

We prepared a microfluidic apparatus for the fabrication of pH-responsive microfibers, and Figure 1 illustrates the schematics of apparatus. Into the sample-inlet port, we introduced the polymerizable sample fluid (a mixture of 85 wt-% 4-hydroxybutyl acrylate (4-HBA), 11 wt-% acrylic acid (AA), 1 wt-% ethyleneglycol dimethacrylate (EGDMA), and 3 wt-% 2,2-dimethoxy-2-phenyl-acetophenone (DMPA)), and into the sheath-inlet port, we

introduced the immiscible non-polymerizable sheath fluid (25% PVA). Fiber formation resulted from the competition between surface tension and shear forces generated at the junction of the two immiscible fluids. They were exposed to UV light (365 nm, Novacure, Photonic Solutions Inc.). Then the moving fibers polymerized, and the solidified microfibers extruded out the outlet pipette.

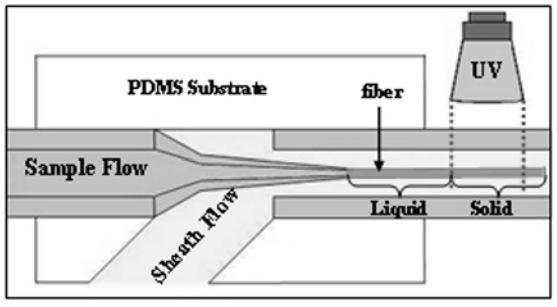
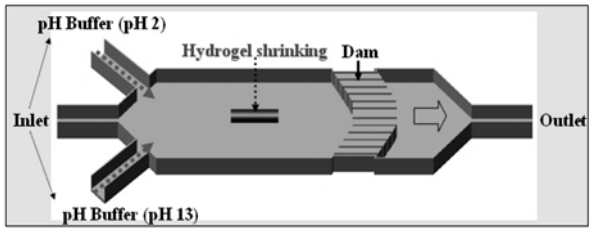
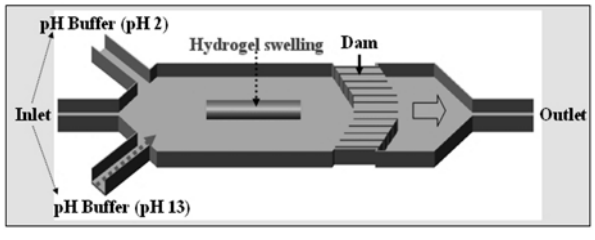


Fig. 1 Schematic diagram of pH-responsive microfibers production system

To examine the volume-transition properties of the pH-responsive microfibers, we fabricated the PDMS-based microfluidic test device, and its schematic diagram is illustrated in Figure 2. This device consists of three inlet ports, a micro-dam that holds the microfiber inside the channel, and one outlet port. The central inlet port supplied water for the rinsing of the channel, and the basic and the acidic solutions were introduced through the other inlets ports. For the injection of fluids, 3 syringe pumps were employed.



(a)



(b)

Fig. 2 Schematic of microfluidic device for tests of (a) the shrinkage and (b) swelling properties of the pH-responsive microfibers.

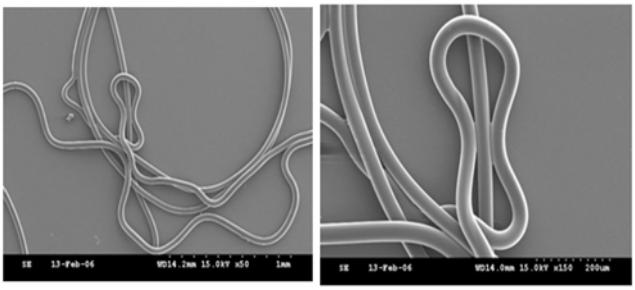
By making alternating additions of the basic and the acidic solutions, we measured the degree of swelling and shrinking quantitatively, and we calculated the swelling ratio, which reflects the degree, according to equation (1):

$$SwellingRatio(\%) = \frac{(Volume_t - Volume_{t0})}{Volume_{t0}} \times 100, \quad (1)$$

where $Volume_{t0}$ is the volume of each microfiber at the first equilibrium state and $Volume_t$ is the volume of each microfibers at certain times after the pH change. Microfiber morphology changes according to pH variation were monitored under a light microscope that featured a CCD image-capturing system. Images of the fibers were captured periodically, and the diameter was digitally measured with Photoshop 7.0.

III. Result and Discussions

The pH sensitive microfibers were successfully produced via 'on the fly' photopolymerization. Figure 3 illustrates the scanning electron microscope (SEM(S-4300, Hitachi)) image of microfibers. We prepared solutions that had different concentrations of AA (Table 1). And FTIR spectroscopy was used to investigate the polymerized microfiber and the FTIR spectrum for polymerized microfibers with different AA concentrations is demonstrated in Figure 4. The absorption bands of carbonyl, carboxyl and hydroxyl group in the AA appeared at 1715 cm-1, 2950 cm-1 and 3500 cm-1, respectively. As the concentration of AA increased, these bands increased. In these bands, the sharp absorption band for carbonyl group at 1715 cm-1 attributed to the C=O strong stretching vibration due to the existence of C=O within each monomers (4-HBA and AA) and crosslinker (EGDMA).Especially, the absorption band for the vinyl group of each monomer was not observed at 1645 cm-1. No band at 1645 cm-1 indicated that the vinyl group of monomers was disappeared completely due to the photopolymerization of 4-HBA and AA and the crosslinking with EGDMA. This indicated that each monomer was synthesized crosslinked co-polymer successfully during 'on the fly' photopolymerization process



(a) (b)

Fig. 3 (a) The scanning electron microscope (SEM) image of the microfibers(x 50), (b) The SEM image of the microfiber(x 150)

Table 1 Microfiber compound and concentration

Solution No.	Compound and Concentration (wt %)			
	4-HBA	DMPA	EGDMA	AA
Solution 1	90	3	1	6
Solution 2	85	3	1	11
Solution 3	74	3	1	22

- Monomer : 4-HBA (4-hydroxybutylacrylate)
- PI (Photoinitiator) : DMPA (2,2-dimethoxy-2-phenylacetophenone)
- Crosslinker : EGDMA (ethyleneglycoldimethacrylate)
- AA (acrylicacid)

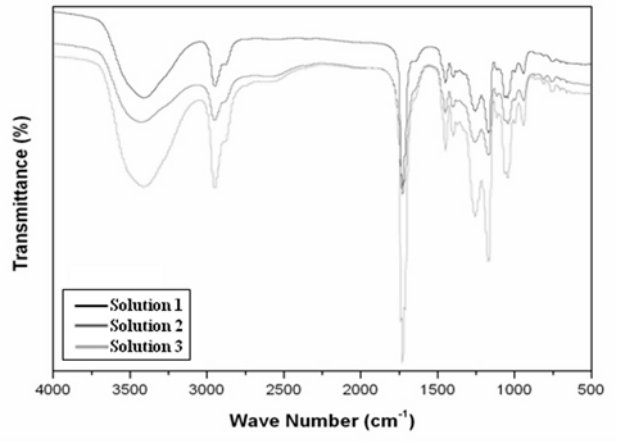
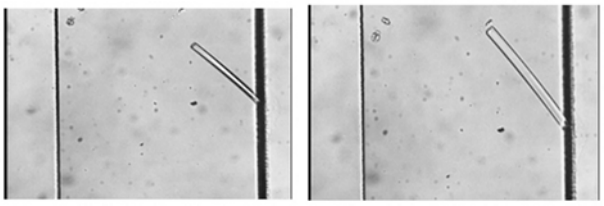


Fig. 4 FTIR spectra of the microfibers fabricated through the use of solution #1, solution #2, and solution #3.

We have observed the swelling and the shrinking motions of fabricated microfibers. Figure 5 illustrates the micrograph of microfibers that were placed in the microfluidic test channel. Into the inlets, the basic (pH 13) and the acidic (pH 2) solutions were introduced respectively. Owing to microfluidic phenomena (laminar flows due to a low Reynolds number (Re≒ 0.5)), one microfiber in the basic solution was swollen, while the microfiber in the acidic solution was shrunken.



(a) (b)

Fig. 5 The swelling and shrinking motions of the fabricated microfibers (100 μm). (a) The change in shape that occurs at the appearance of the acidic solution, (b) The recovery of shape that occurs at the appearance of the basic solution.

We measured volume transition relative to pH changes and, therein, used selected microfibers that had diameters of 50, 80, and 100 μm. The volume of each microfiber exhibited large changes to the variation of pH value. We assume that these responses are mainly due to the size of the microfibers in figure 6. The swelling ratios increased greatly when the size of microfibers was small. The reason for this pattern seems to be that the polymer network's prevents the deep penetration of ions into the larger microfiber. Shape is also an important factor in the volume transition of hydrogel, and we examined the effect of shape.

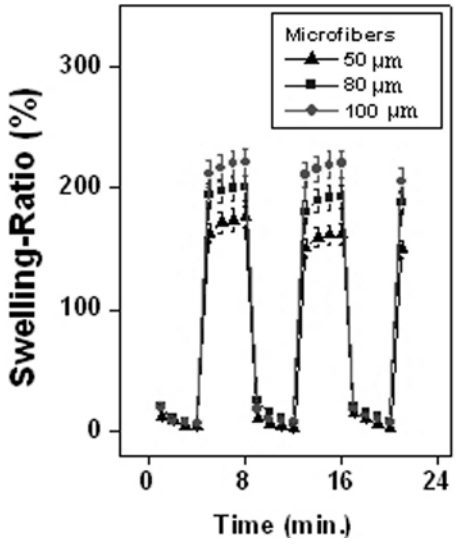
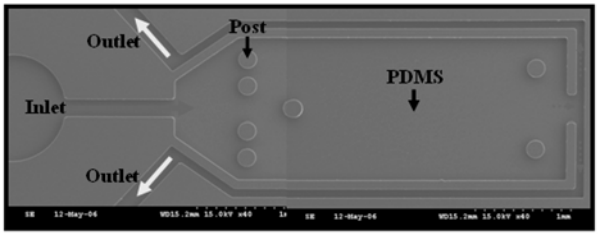
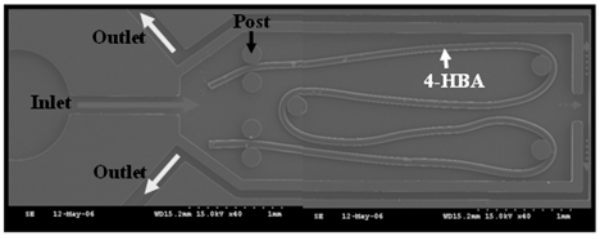


Fig. 6 The swelling ratio of the microfibers (50, 80, 100 μm).

Figure 7(a) shows the scanning electron microscope image (SEM) and the diameter of the microfibers (100 μm) was determined. This artificial device (depth 200 μm) consists of one inlet port (width 200 μm), a microposts (200 μm) that holds the microfiber inside the channel, and one outlet port. Figure 7(b) demonstrates the SEM image was inserted a microfiber in the artificial device. The basic and the acidic solutions were introduced through the inlet port. For the injection of fluids, 2 syringe pumps were employed.



(a)



(b)

Fig. 7 SEM image of fabricated artificial device. (a) non-inserted a microfiber in the artificial device, (b) inserted a microfiber in the artificial device.

IV. Conclusions

In this paper, we have fabricated pH-responsive flexible microfiber using microfluidic chip and 'on the fly' photopolymerization method, and we characterized their mechanical and swelling properties. We have measured the swelling properties according to pH variation. The PDMS based test apparatus was prepared, and we inserted the microfiber and measured the volume transitions. The shrinking and the swelling motions were measured according to the different sized (50, 80, 100μm) fibers to investigate the size effect. The effects of acrylic acid (AA, pH sensitive monomer) concentration were examined also. As the fibers' diameter increases, the response of volume transition was slow, and higher AA showed larger volume expansion to the application of basic solution. We have measured the elasticity of microfiber according to AA concentration (weight %: 6, 11, and 22). The elasticity at the fiber having less AA concentration was larger, and this indicates that the fiber having lower AA concentration is softer. The advantages of our fabrication method are as follows; 1) the process is simple and cost effective, 2) we can functionalize the fiber and this can be applied to diverse microdevices such as sensors or actuators, 3) the size can be easily altered via the regulation of flow rate. Here, we showed the fibers' mechanical properties, and we expect that the microfiber can be applied to the fabrication of artificial muscle

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